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SILVER CATALYSED LEACHING OF CHALCOPYRITE ORE
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A process for bioleaching of chalcopryite ore wherein the chalcopryite ore is treated with silver prior to bioleaching. In one aspect, the crushed chalcopryite ore is agglomerated in the presence of silver which deposits on the agglomerated ore as solid layer so that the silver is uniformly distributed throughout the agglomerated particles. In another aspect, silver may be applied to chalcopryite ore in the absence of an agglomeration medium by percolating a solution of silver ion through a body of the ore wherein silver is thoroughly disseminated throughout the ore.

<p>99-229777/20 D16 M25 MIMH- 97.07.31 MIM HOLDINGS LTD 97.07.31 97AU-008353 (99.02.11) C22B 3/18, 15/00 *AU 9878560-A</p>	<p>Process for bioleaching chalcopyrite ore comprises treating ore with silver and bioleaching ore body to oxidize ferrous ion C99-067687 Addnl. Data: CANFELL A J, WINBORNE A, GREENFIELD F UNIV QUEENSLAND (UYQU) 98.07.30 98AU-078560</p>
<p>D(5-A3A, 5-A4, 5-C) M(25-B, 25-G8)</p> <p>comprising the chalcopyrite ore being placed on an impermeable/semi-permeable support e.g. geotextile membrane or clay or applied to <i>in situ</i> leaching of copper ore bodies comprising forming several wells on either side of an existing body ore and treating with silver solution.</p> <p><u>ADVANTAGE</u> Copper may be extracted from chalcopyrite ore at higher yields and more rapidly than conventional techniques. The costs of reagents is reduced. Results of experiments demonstrated that the addition of silver had a significant positive effect on the bacterial leach of chalcopyrite. The copper extraction was improved from 10% (without silver) to 85% (with 200 mg Ag/kg ore) in 25 days of leaching.</p> <p><u>DESCRIPTION OF DRAWING</u> The figure illustrates the comparison in bacterial leaching of chalcopyrite in shake flask in the presence and absence of silver.</p> <p><u>EXAMPLE</u> A solution containing 0.25 g/l (NH₄)₂SO₄ and 0.05 g/l K₂HPO₄ AU 9878560-A+</p>	<p><u>NOVELTY</u> The bioleaching method comprises treating a body of chalcopyrite ore with silver, uniformly distributed throughout ore body and bioleaching the body of ore to oxidize ferrous ion to ferric ion.</p> <p><u>USE</u> The process is applied to stope leaching where the chalcopyrite ore is leached <i>in situ</i> by the provision of underground shafts located under the ore body and silver is passed through the ore body from the top. The chalcopyrite ore is removed from a stope, crushed to a required particulate size prior to the agglomeration in the presence of silver and subsequently transferred to the stope prior to bioleaching (all claimed). The process also may be applied to a heap leach process</p>

was used as the leaching solution and was adjusted to the desired pH with sulfuric acid. A mixed culture was actively maintained in a slurry containing 5% (w/v) chalcopryite ore in the leach solution above pH 1.6 and 32 °C. The culture contained *Leptospirillum ferrooxidans*, *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans*, *Sulfobacillus thermosulfidioxidans*, *Thiobacillus caldus* and *Acidiphilium cryptum*. The shake flask tests were performed in 250 ml Erlenmeyer flasks containing 100 ml leach solution prepared from Milli-Q grade water. Inoculation was from an active, mixed culture at 5% v/v and charged with 5% w/v chalcopryite ore and kept at pH 2.0 by the addition of sulfuric acid. The flasks were kept in an orbital shaker rotating at 100 rpm at 37 °C and evaporative losses were determined by weight and made up with Milli-Q water. Polyethylene columns were used for small column leaches, jacketed and maintained at 32 °C. They were charged with 1.0 kg chalcopryite ore and the ore was wet screened and sized with narrow ranges especially, 212-425 µm, 833-1168 µm and 2.36-4.70 mm. Leach solution was pumped through the column at 10 l/m²/hour from a 1.0 l reservoir. The discharge of the column was directed back to the reservoir. The solution in the reservoir was aerated and kept at pH 2.0 by the addition of sulfuric acid. The solution was inoculated (at 5% v/v) and evaporative losses were determined by volume and made up with Milli-Q water. The silver

catalyst was mixed with the ore before the column was charged. Ferrous ion was measured by titration with 0.01 M KMnO₄ solution assays for Cu, Fe (total), Mg and Ca using spectroscopy. Solid assays were performed using standard digest and assaying techniques. Bacterial counts were performed using oil immersed lens and Thoma chamber. The composition of leach residues was investigated using X-ray diffraction and optical mineralogy.

TECHNOLOGY FOCUS

Inorganic Chemistry - Preferred Process: The chalcopryite ore is mixed with water and/or sulfuric acid or another agglomeration medium in the presence of silver, at 10-500 (especially 20-200) mg Ag⁺/kg. The chalcopryite ore may be treated in the absence of an agglomeration medium by percolating a Ag⁺ (10-500 (especially 20-200) mg/kg) solution through the body of the ore until thoroughly disseminated. The Ag⁺ solution is pumped to the top of a chalcopryite ore heap and then sparged over the ore heap. The silver is mixed with a complexing agent to obtain a complex cation which is applied to the chalcopryite ore. Orthophosphate or Milli-Q water is mixed with silver ion prior to application to a body of chalcopryite ore which is especially crushed prior to treatment with silver to have a particle size 1 inch to -10 mesh

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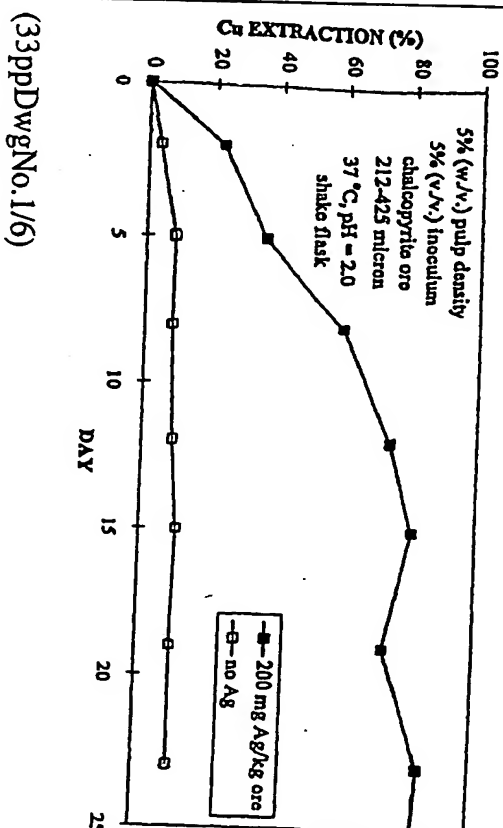
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size or from 6.35-12.5 mm. The leaching solution is pumped to the ore body after passing through a PLS (pregnant leaching solution) dam which is also in flow communication with the ore body so that leaching solution enriched in copper values after discharge from the ore body is transferred to the PLS dam (especially in flow communication with an electrowinning solvent/extraction zone for the copper extraction). The ore body is in flow communication with a PLS dam as well as a raffinate pond which are interconnected by the electrowinning solvent/extraction zone.

Organic Chemistry - Preferred Process: The complexing agent is ammonia, pyridine, ethylene diamine, olefins, other organic amines or especially thiourea.

Biotechnology - Preferred Process: Bioleaching takes place in the presence of sulfuric acid and water and is initiated at pH 1.5-2.0 and at 27-37 °C to facilitate propagation of bacteria. The bacteria for the oxidation of ferrous ion is *Leptospirillum ferrooxidans*, *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans* or *Sulfobacillus thermosulfatoidans*. A bacterial inoculate is added directly to an ore body prior to passage of leaching solution and is combined with the leaching solution through a body ore. The leaching solution passes

through a separate oxidation zone which contains bacteria prior to passage through an ore body. The bacterial inoculate is added to the PLS dam or raffinate pond.



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AUSTRALIA

Patents Act 1990

**ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT**

Invention Title: "SILVER CATALYSED LEACHING OF CHALCOPYRITE ORE"

The following statement is a full description of this invention, including the best method of performing it known to us:-

TITLE

"SILVER CATALYSED LEACHING OF CHALCOPYRITE ORE"

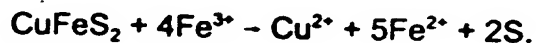
FIELD OF THE INVENTION

THIS INVENTION relates to a chalcopryite leaching process.

BACKGROUND OF THE INVENTION

Chalcopryite is an extremely stable mineral having the formula CuFeS_2 which is resistant to leaching as discussed in Brierley, 1978, CRC Critical Review of Microbiology 6 207-262 and Brierley, pp 372-379 in a reference entitled "*Gold and Copper Ore/Concentrate Bioleaching*" published at the Proceedings of the International Symposium 33rd Annual Conference of Metallurgists of CIM, Canada, 1994, B. Harris and E. Krause, Eds. The bacterial leaching of chalcopryite ore is a particularly slow and incomplete process even when solution parameters such as pH, temperature, nutrients and inoculum are optimized. For example, the bioleach of a typical chalcopryite ore in percolating columns gave only 3.5% yield in 80 days as discussed in Ahonen *et al.*, 1993, Biohydrometallurgical Technologies, 571-578, A. E. Toma, J. E. Way and V. L. Lakshmanan, Eds.

At present, therefore, leach rates and overall conversion to copper in regard to chalcopryite for industrial or commercial applications are uneconomic. ~~The reason for unsatisfactory leach rates is generally attributable to the formation of an elemental sulphur layer which is impermeable to diffusion of reactants and/or products and thus inhibits leaching as described in Toma *et al.*, Copper 91, 73-85, W. C. Cooper, D. J. Kemp, G. E. Lagos and K. T. Tan, Eds.~~ The sulphur layer is formed in accordance with the equation:-



The incomplete leaching of chalcopryit may also be due to partial oxidation of chalcopryite to form an unreactive, intermediate metal sulphide compound as described in Hackl *et al.*, 1995, Hydrometallurgy

39 25-48.

Prior attempts to overcome the recalcitrance of chalcopyrite to leaching have included the use of thermophilic bacteria, as described in Le Roux *et al.*, 1988, *Biohydrometallurgy* 305-317; the use of catalytic monovalent ions as described in Ahonen *et al.*, 1989, *Biohydrometallurgy* 25-34, Proceedings of the International Symposium, Jackson Hole, Wyoming, J. Salley, R. G. L. McCreedy and P. L. Wickliffe, Eds.; and redox control as discussed in Ahonen *et al.*, 1993, *supra*. However, as described in Brierley, 1994, *supra*, none of these methods have produced any commercial solution to overcoming the recalcitrance of chalcopyrite to leaching. In fact, it was stated in Brierley, 1994, *supra*, that "making bioleaching a viable process for chalcopyrite treatment will require innovative control of chemical, electrochemical and biological activities."

One of the few encouraging advances in biological leaching of chalcopyrite is the use of silver catalysis wherein silver is added to the leaching medium. This was first reported in McElroy *et al.* in U.S. Patent 3856913 and has been the subject of many publications since then. However, no industrial or commercial application has occurred to date mainly due to the high cost of the silver reagent. The mechanism of the catalysis of chalcopyrite bioleaching by silver catalysis is not clear. The most popular theory is formation of the so-called silver sulphide layer, which has been endorsed by many authors including Ahonen *et al.*, 1989, *supra*; Ballester *et al.*, 1990, *Hydrometallurgy* 23-221-235 and Barriga-Mateos *et al.*, 1993, *Biorecovery* 2 195-218. The silver sulphide layer continually forms as discussed in Ahonen *et al.*, 1990, *Minerals Engineering* 3(5) 437-445 and is re-oxidized as discussed in Ahonen *et al.*, 1993, *supra*. However, when the silver sulphide layer is re-oxidized, chalcopyrite is solubilized. Elemental sulphur still forms but in so doing, it forms a porous layer which allows diffusion of reactants and products and so does not stop the leaching.

~~The role of micro-organisms in the leaching of chalcopyrite in~~

~~combination with silver catalysis as described above is to oxidize ferrous ion, regenerating ferric ion, i.e.~~



5 Ahonen *et al.*, 1990, *supra*, performed silver catalysed bacterial leaches of chalcopyrite ore in columns. Initially, the columns were operated without silver, resulting in typically slow leach rates. When silver was added, the rate of copper extraction increased ten-fold. However, the effect was transient and the rate of extraction eventually
10 returned to its original value.

The use of silver catalysis in leaching of chalcopyrite is also discussed in U.S. Patents 3886257, 3974253 and 4571387 wherein silver is added to the leaching medium which may also contain aqueous sulphuric acid and a bacterial inoculate.

15 Heap leaching of copper ores is well known and reference may be made, for example, to Robles *et al.*, in an article entitled "*Recent Experience in Bacterial Assisted Heap Leaching of Copper Ores in Chile*" which was reported in "BIOMINE 1994" in a seminar conducted by the Australian Mineral Foundation in Perth on September 19-20, 1994. This
20 reference describes ~~currently known heap leaching procedures~~ which usually comprise the following steps:-

- (i) initial crushing of the ore to produce particles having nominal maximum sizes between 6.35-12.50 mm;
- (ii) agglomeration of the crushed ore in a rotating drum
25 with agglomeration medium which may comprise water combined with sulphuric acid. Agglomeration provides an ore heap with long term high liquid and gaseous permeability and ~~self-generation of ferric ion~~. Raw water or raffinate solution (i.e. recycled copper leach liquor) may be used as the agglomeration
30 medium or concentrated sulphuric acid may be used

when there are some mixed oxide/sulphid ores in the crushed ore;

- (iii) stacking of the agglomerated ore on a leach membrane with a 1-2° slope wherein leaching solution is applied to the ore heap by the use of drippers or wobblers at the rate of 5-15 l/hr/m².

In the aforementioned Robles *et al.* reference, the copper ores which are described as the most amenable to heap leaching include chalcocite (Cu₂S) and covellite (CuS). To date, however, it has not been possible to subject chalcopyrite to a heap leaching process since chalcopyrite has been highly resistant to leaching for the reasons set out above.

Reference may also be made to U.S. Patent 5332559 which also describes conventional heap leaching processes. In this reference, use is made of an acid resistant polymeric agglomeration aid having an acid resistance at a pH of between 1.3-2.5 which apparently makes agglomeration more efficient. Reference is also made to chalcopyrite (incorrectly referred to as cobaltite) in this reference as being leachable in accordance with the process of U.S. Patent 5332559. However, this assertion must be viewed with a great deal of suspicion since there is no experimental support in U.S. Patent 5332559 to provide basis for this assertion and such assertion is contrary to the teachings in the literature references described above.

Reference may also be made to U.S. Patent 5246486 which describes a heap leaching process wherein precious metals dispersed or occluded within a heap of mineral-ores as pyritic or arsenopyritic sulphides are freed by forming particulates from the ore particles with a bacterial inoculate which forms sulphides and/or elemental sulphur by biooxidation.

SUMMARY OF THE INVENTION

It therefore is an object of the invention to provide a process

for bioleaching of chalcopyrite whereby copper may be extracted at satisfactory yields.

Surprisingly, it has now been discovered that rapid bioleaching of chalcopyrite can now occur whereby leaching of chalcopyrite can occur if the chalcopyrite ore is treated with silver prior to leaching.

Thus, the process of the invention includes the following steps:-

- (i) treating a body of chalcopyrite ore with silver so that silver is uniformly distributed throughout the body of ore; and
- (ii) subsequently bioleaching the body of ore to oxidize ferrous ion to ferric ion.

In a first embodiment of the invention, the bioleaching process includes an agglomeration step wherein the chalcopyrite ore is mixed with water and/or sulphuric acid or other agglomeration medium in the presence of silver where the concentration of silver suitably in the form of Ag^+ included in the agglomeration medium is from 10-500 mg/kg of ore and more preferably from 20-200 mg Ag^+ /kg of ore. It is preferred that the concentration of silver does not exceed 500 mg/kg of ore because concentrations in excess of this amount (i) is uneconomic and also may not be satisfactory in use; and (ii) may adversely effect the bacteria utilized in the subsequent bioleaching of the ore.

However, in a second embodiment of the invention, if the bioleaching process of the invention excludes an agglomeration step, then silver in the above concentrations may be applied prior to leaching. This may occur, for example, by percolating an Ag^+ solution through a body of ore whereby the Ag^+ solution is thoroughly disseminated throughout the ore. This may take place by pumping the Ag^+ solution to the top of the ore heap and then sparging the silver solution over the top of the ore by use of sprinklers, jets or wobblers.

Preferably the silver is mixed with a complexing agent such as thiourea wherein silver in the form of a complex cation (i.e. $\text{Ag}[\text{CS}(\text{NH}_2)_2]^+$) may be applied to the body of the ore. Alternatively, the silver may be treated with other complexing agents, such as ammonia, to give silver ammine cations, pyridine, ethylene diamine, olefins or other organic amines. Alternatively, the addition of orthophosphate or Milli-Q water may enhance uniform distribution of silver throughout the ore body. Recovery of the silver from the body of ore may be achieved by the use of thiourea as a washing agent or any of the other complexing agents.

The chalcopryite leaching process of the invention may be applied to heap leaching of chalcopryite wherein chalcopryite ore is initially crushed to produce particles which facilitate a satisfactory rate of bioxidation as is known in the art. The size of such particles is variable and may range from one inch to minus ten mesh size as described in U.S. Patent 5332559. Alternatively, a size distribution may range from 6.35-12.5 mm as described in the BIOMINE 1994 reference referred to above.

Proper ore crushing and particle size are achieved as described in the aforementioned references or in Perry's "Chemical Engineer's Handbook", 4th Edition, 1973.

Following crushing, the ore may then be agglomerated in any suitable manner as is known in the art and as described in the BIOMINE 1994 reference, which disclosure is incorporated herein by reference, or U.S. Patent 5332559, which disclosure is herein incorporated by reference, or U.S. Patent 5246486, which disclosure is herein incorporated by reference, wherein the agglomeration medium may include water, a solution of sulphuric acid or a polymeric species as described in U.S. Patent 5332559, such as an acid resistant microbial bioxidant compatible, water soluble vinyl addition polymer which may be selected from homopolymers, copolymers, terpolymers or higher polymers of a compound of general formula



where R is a nitrile, an amide, a carboxyl radical COOR^1 where R^1 is a lower alkyl radical preferably having from 1-4 carbon atoms and the water soluble salt thereof. The agglomeration acid may additionally include a surfactant as described in U.S. Patent 5332559.

Various other agglomeration agents are described in U.S. Patents 5077021, 5077022, 3418237, 4875935 and 4898611 which disclosures are also incorporated herein by reference.

However, in accordance with the first embodiment of the invention, the crushed ore is agglomerated in the presence of silver which preferably is in the form of Ag^+ which may deposit on the agglomerated particles of the ore as a solid layer so that the solid silver is comprehensively and uniformly distributed throughout the agglomerated particles.

In a preferred embodiment, the invention is particularly directed to a heap leach process wherein chalcopyrite ore is placed on an impermeable/semi-permeable support such as a geotextile membrane or clay. A suitable biological lixiviant solution is reticulated to the top of the heap of chalcopyrite ore by sprinklers, drippers or some other sparging apparatus after initial treatment of the heap of ore with silver as described above. The lixiviant trickles through the ore and leaches with the desired mineral, i.e. copper, thereby releasing the copper values from the ore as calcium sulphate. The copper may then be recovered from solution by solvent extraction or electrowinning.

The process of the invention may also be applied in *in-situ* leaching of copper ore bodies where a plurality of wells may be formed on either side or around an existing body of ore by blasting, drilling or other suitable method and the ore may be initially treated with silver, as described above, and may be disseminated throughout the body of ore by percolation, irrigation or other suitable means. Usually, the passage of silver in solution occurs horizontally through the body of ore from the peripheral wells on either side or which surround the body of ore.

The process of the invention may also be applied to stope leaching where an ore body may be leached *in-situ* by the provision of underground shafts located under the ore body and the silver passed through the ore body from the top thereof by use of irrigation methods so that the silver is comprehensively and uniformly distributed throughout the body of ore. In the case where the ore is removed from a stope, it is crushed to the required particulate size, agglomerated in the presence of silver as described above and then transferred to the stope prior to leaching.

Following passage of silver through the body of chalcopyrite ore, the ore may be leached by any suitable method as is known in the art. Suitably the leaching takes place with sulphuric acid and water. Ferric sulphate may also be added. Ferrous sulphate may also be utilized. The pH may be between 1.5-2.0 when leaching is initiated. The leaching operation suitably takes place at a temperature which facilitates the use of bacteria and this may be from 27-37° and more suitably 32°C.

~~The bacteria for the bioleaching process in relation to oxidation of ferrous ion, regenerating ferric ion, may be from any suitable source which could be ubiquitous (i.e. naturally present in the ore) and such as *Leptospirillum ferrooxidans* as well as a sulphur oxidizer, such as *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans* and *Sulfobacillus thermosulfidioxidans* may also be utilized.~~

Suitable bacteria for bioleaching of sulphide ore are well known and are described, for example, in U.S. Patents 5246486, 4822413 and 5332559, the disclosure of which is totally incorporated herein by reference.

Preferably the leaching process may include the situation where the bacterial inoculate is added directly to the ore body prior to passage of leaching solution through the ore body or more suitably combined with the leaching solution. Alternatively, the leaching solution may pass through a separate oxidation zone which contains the bacteria.

Preferably the leaching process is a cyclic one so that leaching solution is pumped to the ore body after passing through a PLS (Pregnant Leaching Solution) dam or pond which also is in flow communication with the ore body so that leaching solution enriched in copper values after discharge from the ore body is transferred to the PLS dam. The PLS dam may also be in flow communication with an electrowinning/solvent extraction zone whereby copper may be extracted in any suitable manner as is known in the art and as described, for example, in a reference entitled *"The Chemistry of Metals Recovery using LIX Reagents"* published by Henkel Corporation, which is herein incorporated by reference.

In an alternative situation, the ore body may be in flow communication with a PLS pond or dam as well as a raffinate (copper lean liquor) pond or dam which are interconnected by the electrowinning/solvent extraction zone.

It will also be appreciated that the bacterial inoculate can be added to the aforementioned circuits at any suitable location, such as the PLS pond or raffinate pond.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph comparing the bacterial leaching of chalcopyrite in a shake flask as described in the Experimental section carried out in the presence of silver and also carried out in the absence of silver;

FIG. 2 is a graph comparing the bacterial leaching of chalcopyrite in a column as described in the Experimental section carried out in the presence of silver and also carried out in the absence of silver;

FIG. 3 is a graph comparing the bacterial leaching of chalcopyrite in a column as described in the Experimental section comparing the situation wherein silver is added to the ore prior to leaching and when silver is incorporated in the leaching medium;

FIG. 4 is a schematic view of the leaching apparatus as

applied to a column of chalcopyrite ore;

FIG. 5 is a graph of leaching of chalcopyrite ore as described in the Experimental section comparing leaching wherein silver has been previously incorporated in the ore and leaching in the absence of silver having regard to certain particulate sizes of the ore; and

FIG. 6 is a graph of leaching in a column of chalcopyrite ore which has been crushed to sizes of 6 mm and 12 mm and which also has been agglomerated with or without the addition of silver catalyst.

EXPERIMENTAL

MATERIALS AND METHODS

Chalcopyrite ore

The chalcopyrite ore was sourced from an underground mine in North Queensland. The chemical and mineralogical composition of the ore is given in TABLE 1 (the mineral fractions were estimated from the chemical analysis). The chalcopyrite occurs in micro-fractures of up to 100-200 μm that interconnect along fracture lines within a quartz matrix. The ore also contains dolomite ($(\text{Ca/Mg})\text{CO}_3$) and pyrite (FeS_2) with minor amounts of chlorite, barite, pyrrhotite and cobaltite.

Leach solution

A solution containing 0.25 g/l $(\text{NH}_4)_2\text{SO}_4$ and 0.05 g/l K_2HPO_4 was used for all tests. This was found to have sufficient nutrients to maintain adequate cell physiology. The advantage of using a small amount of nutrients is two-fold: The reagent cost of the operation is reduced and the amount of mono-cations in solution, which exacerbate jarosite precipitation, is reduced. The solution was adjusted to the desired pH with sulphuric acid.

Bacteria

A mixed culture was sourced from site and actively maintained in a slurry containing 5% (w/v) chalcopyrite ore in the leach solution above at pH = 1.60 and temperature 32°C. The culture contained *Leptospirillum ferrooxidans*, *Thiobacillus ferrooxidans*, *Thiobacillus*

thioxidans, *Thiobacillus caldus*, *Sulfobacillus thermosulfidioxidans* and *Acidiphilium cryptum*. This culture represents a diverse cross-section of bacteria and was used for all bioleaching testwork.

Shake flasks

- 5 The shake flask tests were performed in 250 ml Erlenmeyer flasks. The flasks contained a total of 100 ml of leach solution prepared from milli-Q grade water. Inoculation was from an active, mixed culture at 5 % (v/v). The flasks were charged with 5% (w/v) of chalcopryite ore and kept at a pH of 2.00 by the addition of sulphuric acid. The flasks were
) kept in an orbital shaker rotating at 100 rpm, the temperature was maintained at 37°C. Evaporative losses were determined by weight and made up with milli-Q water.

Small columns

- 15 Polyethylene columns of dimensions 64 x 300 mm were used for small column leaches. The columns were water jacketed and maintained at 32°C. Columns were charged with 1.0 kg of chalcopryite ore. The ore was wet screened and sized within narrow ranges. The size ranges used were 212-425 µm, 833-1168 µm and 2.36-4.70 mm.

- 20 Leach solution was pumped through the column at 10 l/m²/h from a 1.0 l reservoir. The discharge of the column was directed back into the reservoir. The solution in the reservoir was aerated and kept at a pH of 2.00 by the addition of sulphuric acid. The solution was inoculated (at 5% v/v); evaporative losses were determined by volume and made up with Milli-Q water. Where required, silver catalyst (200 mg Ag/kg ore) was
 25 mixed with the ore before the column was charged.

Large columns

- 30 Leaching was performed in a constant temperature room which was maintained at 32°C. The columns were constructed from polyethylene of dimensions 140 mm x 2.0 m. Each column was charged with 40.0 kg of chalcopryit ore. A quartz layer was added to the top to ensure even solution distribution and to the bottom to stop fines falling

through.

Leach solution was pumped through the column at 10 l/m²/h from a 20.0 l reservoir. The discharge of the column was directed back into the reservoir. The solution in the reservoir was aerated and kept at a pH of 1.60 by the addition of sulphuric acid. Initially a strong sulphuric acid solution was used to solubilize dolomites in the ore. When the pH of the discharge had stabilised, the solution was inoculated (at 5% v/v) and leaching commenced. Evaporative losses were determined by volume and made up with distilled water.

Ore crush sizes of p80 = 6 mm and p80 = 12 mm were trialed. The agglomeration was also performed with and without the addition of silver catalyst. The ore was agglomerated with dilute sulphuric acid with silver being added during agglomeration to ensure an even silver distribution throughout the ore. The silver was added as AgNO₃ solution to give 200 mg Ag/kg ore.

Copper from the reservoir was removed using batch solvent extraction when the copper tenor reached 4 g/l. The extractant was 20% Acorga M5640 with Shellsol 2046 as diluent.

Assays

Ferrous ion was measured by titration with 0.01 M KMnO₄. Solution assays for Cu, Fe(total), Mg and Ca were performed using Atomic Absorption Spectroscopy. Solid assays were performed using standard digest and assaying techniques. Bacterial counts were performed using an oil-immersed lens and a Thoma chamber. The composition of leach residues was investigated using X-ray diffraction (XRD) and optical mineralogy. For XRD, the samples were ground and top mounted in a Philips vertical diffractometer using copper K α radiation. Optical mineralogy was performed on polished thin sections.

RESULTS

Shake flasks

The addition of silver had a significant, positive effect on the

bacterial leach of chalcopyrite (FIG. 1). The copper extraction was improved from 10% (without silver) to 85% (with 200 mg Ag/kg ore) in 25 days of leaching. This illustrates the enormous potential of silver catalyst for the enhancement of chalcopyrite bioleaching.

There have been reports on other cations that have had a similar catalytic effect as silver when applied to the bioleach of chalcopyrite. In descending order of effectiveness these are Hg(II), Co(II), Bi(III) and As(V) (Ballester *et al.*, 1990, *Hydrometallurgy* **23** 231-235). Finely ground graphite has also enhanced the bioleaching of chalcopyrite (Ahonen *et al.*, 1989, *supra*). The cations and graphite were trialed in this study, however, no significant catalytic effect was observed (results not shown).

Small columns

The encouraging result obtained with silver catalysis in shake flasks was applied in ore in 300 mm high columns. A bioleach was performed on ore screened from 2.36-4.70 mm with 0 and 200 mg Ag/kg ore with the silver being added to the leach solution. The results are shown in FIG. 2. Silver has a significant positive effect on the bioleaching of chalcopyrite ore in columns.

At the end of the test, samples were taken from the top, middle and bottom of each column for assaying. The column with silver catalysis had an uneven distribution of silver, most had precipitated at the top of the column and virtually no silver was present at the bottom of the column. The copper extraction was correspondingly high at the top of the column and negligible at the bottom of the column.

To test how important the method of silver addition is, two more silver catalysed columns were operated. One column had the silver added to the leach solution (as was done in the column in FIG. 2). The other column had the ore mixed in a silver solution before loading in the column. This latter column, where the silver was added to the ore, should have a homogenous distribution of silver throughout the ore. The results

of this test is illustrated in FIG. 3. As can be seen, the effect of an even silver distribution (adding the silver to the ore) is significant, the copper extraction was increased from 50% to 90% for the ore size 212-425 μm . The implications are that silver must be added evenly to the ore before the column (or stope) is loaded. The obvious way to do this is during agglomeration.

Chemical assays, XRD and optical mineralogy was performed on the leach residues from the shake flask and small column experiments. The solid residues from both shake flask and small column tests had the same reaction products. These were jarosite ($\text{XFe}_3(\text{SO}_4)_2(\text{OH})_6$ where $\text{X} = \text{Na}^+, \text{K}^+, \text{NH}_4^+, \text{H}_3\text{O}^+$), goethite ($\text{FeO} \cdot \text{OH}$), elemental sulphur (S^0) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). There were, however, significant differences in the distribution of these products in the residues from each test.

Analysis of shake flask particles revealed that quite a lot of fine jarosite and fine goethite formed which was not attached to the ore particles. This may have formed colloiddally or it may have been broken off the ore particles by the mechanical action of the shake flasks.

Optical mineralogy illustrated that the column ore particles had been coated with goethite (limonite) and jarosite. The coatings were quite thin ($\sim 1 \mu\text{m}$), but appeared impermeable to leach solution. In some samples, the ore was coated by jarosite which then had a second coating of goethite. The initial precipitation of jarosite is favoured because the leach solution has cations from nutrients that enhance jarosite formation. In addition, the pH fluctuates because of carbonate dissolution and a high pH favours jarosite precipitation. As the mono-cations are removed from solution and the pH stabilises at a low value, the formation of goethite is favoured (which precipitates on top of jarosite). The goethite also appeared to form flocs which deposited on the ore surface, however, it was not believed that these contributed significantly to the ore passivation. Gypsum was precipitated between ore particles and in some

cases appeared to replace dolomite *in-situ*.

Large column bioleach

The large columns were operated to test the leaching method on ore sizes that can be economically achieved in the field and in 2.0 m columns to enable a more realistic comparison to an actual stope or heap. The experimental setup used is illustrated in FIG. 4. The ore was agglomerated with an acidic solution. Silver was added (as a solution) during the agglomeration to ensure that silver was distributed evenly throughout the ore.

The results of bioleaching chalcopyrite in 2.0 m columns are shown in TABLE 2 and FIG. 5. The columns were operated for 190 days although leaching stopped at around 160 days for the silver catalysed columns. There was an initial lag of approximately 10 days, during which time the concentration of ferric was negligible. The columns were batched between day 65 and day 90 due to a temporary loss in bacterial activity. Therefore, the effective leaching time is approximately 125 days.

As can be seen, the effect of silver was very significant, increasing the copper extraction from 9% to 66% for 6 mm ore. The leaching of p80 = 12 mm material was also quite high.

The chalcopyrite is located along micro-fractures within the quartz matrix. For large ore particles, some of the chalcopyrite inside the ore particle is virtually inaccessible to leach solution. Samples of the 6 mm and 12 mm ore were subjected to a leach in aqua-regia. The aqua-regia solubilized all of the accessible chalcopyrite. The amount of inaccessible chalcopyrite was 7% for p80 = 6 mm.

A small amount of copper re-precipitated as malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) which was subsequently coated in jarosite. This occurred near gypsum crystals and was attributed to a high local pH at the time of malachite deposition. The malachite did not re-leach when the solution conditions had recovered (i.e. pH reduced) because the jarosite provided an impervious coating.

There was no blocking of the column with fines, visual inspection revealed that the agglomerates held together for the duration of the leach.

The above results indicate that the mechanism of leach cessation is quite complicated and a combination of many factors. The shake flasks illustrate the optimum bioleach solution of chalcopyrite utilizing silver catalysis. The columns illustrate that other facts can limit leaching. For example, a pH profile down the column will cause the deposition of ferric precipitates, such as jarosite and goethite on the ore surface. These precipitates can limit the diffusion of reactants and/or products and stop leaching.

It has been illustrated previously that the method of silver addition to the ore strongly influences the overall conversion of copper from chalcopyrite. In general, an even distribution of silver over the ore is desirable to ensure that all of the ore is equally catalysed. If ore is crushed and packed into a heap or stope, then silver can be added to the ore as it is being handled. The most convenient way to add the silver is as a solution during agglomeration. If the process does not use agglomeration, the silver can be sprinkled on the ore as it is packed.

One of the process options investigated was the *in-situ*, in-stope leaching of chalcopyrite. In this situation, the ore is not handled and hence there is no opportunity to add silver evenly over the ore. It has been illustrated that pumping a silver solution over the ore may not give an even distribution of silver in these circumstances (FIG. 3). This was probably due to the pH profile down the stope, resulting in rapid adsorption of silver as the pH increased. It was reasoned that an agent that complexed with silver, may allow slow adsorption of silver, and hence give an even silver distribution. Silver was mixed with the reagents in TABLE 3 and then pumped through 30 cm columns, packed with fresh chalcopyrite ore as previously described.

After silver concentration in solution had been reduced to <

0.1 ppm, four equidistant samples were taken from top to bottom of the columns, and assayed for silver, the results are illustrated in FIG. 6.

The results indicated that the nutrient medium M1 and thiosulphate are unsuitable for loading silver onto the ore. Any chloride in solution immediately forms a precipitate with silver and results in an uneven distribution of silver over the ore.

Complexation with thiourea gave an excellent distribution of silver. The silver-thiourea bond is very strong, so the adsorption of silver onto the ore was quite slow, resulting in a good distribution. Addition in milli-Q water or with orthophosphate also gave a good distribution of silver.

A suitable operating protocol would be to acid wash the ore until the pH of the outlet is < 4.0 . Then drain the stope and load the silver-thiourea complex. After the silver is loaded, leaching of the ore may commence. The silver-thiourea complex should be made up in a small volume of acidic water which contains negligible chloride ion.

If necessary, the silver can be added at multiple injection points down the stope, although this would increase the capital cost.

TABLES**TABLE 1** Composition of chalcopyrite ore

Cu	0.98
Fe	6.6
Si	31.5
Ca	2.6
Mg	1.6
CuFeS ₂	3.2
FeS ₂	12.3
SiO ₂	67.3
(Ca/Mg)CO ₃	12.0

TABLE 2 Large column bioleach - Summary

L1	6 mm	0	9
L2	12 mm	0	8
L3	6 mm	200	66
L4	12 mm	200	48

TABLE 3 Silver loading tests

Milli-Q grade water	-	-
Nutrient M1	K_2HPO_4 $(NH_4)_2SO_4$ KCl	-
Thiosulphate ion	$S_2O_3^{2-}$	-
Thiourea	$CS(NH_2)_2$	$Ag[CS(NH_2)_2]_3^+$
Orthophosphate	PO_4^{3-}	-

The claims defining the invention are as follows:-

1. A process for bioleaching of chalcopyrite ore which includes the following steps:-

- (i) treating a body of chalcopyrite ore with silver so that silver is uniformly distributed throughout the body of ore; and
- (ii) subsequently bioleaching the body of ore to oxidize ferrous ion to ferric ion.

2. A process as claimed in Claim 1 where chalcopyrite ore is mixed with water and/or sulphuric acid or other agglomeration medium in the presence of silver which is included in the agglomeration medium in a concentration of 10-500 mg Ag^+ /kg of chalcopyrite ore.

3. A process as claimed in Claim 2 wherein the concentration of silver is 20-200 mg Ag^+ /kg of chalcopyrite ore.

4. A process as claimed in Claim 1 wherein the chalcopyrite ore is treated with silver in the absence of an agglomeration medium by percolating an Ag^+ solution through a body of ore wherein the Ag^+ solution is thoroughly disseminated throughout the ore wherein the Ag^+ concentration in the ore is from 10-500 mg Ag^+ /kg of chalcopyrite ore.

5. A process as claimed in Claim 4 wherein the Ag^+ concentration in the ore is 20-200 mg Ag^+ /kg of chalcopyrite ore.

6. A process as claimed in Claim 4 or 5 wherein the Ag^+ solution is pumped to the top of a chalcopyrite ore heap and then sparged over the ore heap.

7. A process as claimed in any preceding claim wherein the silver is mixed with a complexing agent wherein silver in the form of a complex cation is applied to a body of chalcopyrite ore.

8. A process as claimed in Claim 7 wherein the complexing agent is selected from thiourea, ammonia, pyridine, ethylen diamine, olefins or other organic amines.

9. A process as claimed in Claim 8 wherein the complexing

agent is thiourea.

10. A process as claimed in any one of Claims 1-6 wherein orthophosphate or Milli-Q water is mixed with silver ion prior to application to a body of chalcopyrite ore.
11. A process as claimed in any preceding claim wherein the chalcopyrite ore is initially crushed prior to treatment with silver to have a particle size range of one inch to minus ten mesh size or from 6.35-12.5 mm.
12. A process as claimed in Claim 1 applied to *in situ* leaching of chalcopyrite ore bodies wherein a plurality of wells are formed on either side or around an existing body of ore and the ore is initially treated with silver after passage through said plurality of wells to achieve a uniform distribution throughout the ore body before bioleaching of the ore.
13. A process as claimed in Claim 1 applied to stope leaching wherein a chalcopyrite ore body is leached *in situ* by the provision of underground shafts located under the ore body and silver is passed through the ore body from the top thereof.
14. A process as claimed in Claim 2 wherein a chalcopyrite ore body is removed from a stope, crushed to a required particulate size prior to the agglomeration in the presence of silver and subsequently transferred to the stope prior to bioleaching.
15. A process as claimed in any preceding claim wherein the bioleaching takes place in the presence of sulphuric acid and water and is initiated at a pH of 1.5-2.0 and at a temperature of 27-37°C to facilitate propagation of bacteria.
16. A process as claimed in Claim 15 wherein the bacteria includes *Leptospirillum ferrooxidans* for oxidation of ferrous ion.
17. A process as claimed in Claim 16 wherein the bacteria also include sulfur oxidizing bacteria selected from *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans* and *Sulfobacillus thermosulfidioxidans*.
18. A process as claimed in Claim 15 wherein a bacterial

inoculation is added directly to an ore body prior to passage of leaching solution therethrough.

19. A process as claimed in Claim 15 wherein a bacterial inoculate is combined with the leaching solution prior to passage of the leaching solution through a body of ore.

20. A process as claimed in Claim 15 wherein the leaching solution passes through a separate oxidation zone which contains the bacteria prior to passage through an ore body.

21. A process as claimed in Claim 15 wherein leaching solution is pumped to the ore body after passing through a PLS (Pregnant Leaching Solution) dam which is also in flow communication with the ore body so that leaching solution enriched in copper values after discharge from the ore body is transferred to the PLS dam.

22. A process as claimed in Claim 21 wherein the PLS dam is in flow communication with an electrowinning/solvent extraction zone for extraction of copper.

23. A process as claimed in Claim 22 wherein the ore body is in flow communication with a PLS dam as well as a raffinate pond which are interconnected by the electrowinning solvent/extraction zone.

24. A process as claimed in Claim 23 wherein bacterial inoculate is added to the PLS dam or raffinate pond.

25. A process as claimed in the Claim 1 substantially as herein described with reference to the Experimental section.

DATED this thirtieth day of July 1998.

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THE UNIVERSITY OF QUEENSLAND and
MIM HOLDINGS LIMITED.
by their Patent Attorneys,
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ABSTRACT

A process for bioleaching of chalcopyrite ore wherein the chalcopyrite ore is treated with silver prior to bioleaching. In one aspect, the crushed chalcopyrite ore is agglomerated in the presence of silver which deposits on the agglomerated ore as solid layer so that the silver is uniformly distributed throughout the agglomerated particles. In another aspect, silver may be applied to chalcopyrite ore in the absence of an agglomeration medium by percolating a solution of silver ion through a body of the ore wherein silver is thoroughly disseminated throughout the ore.

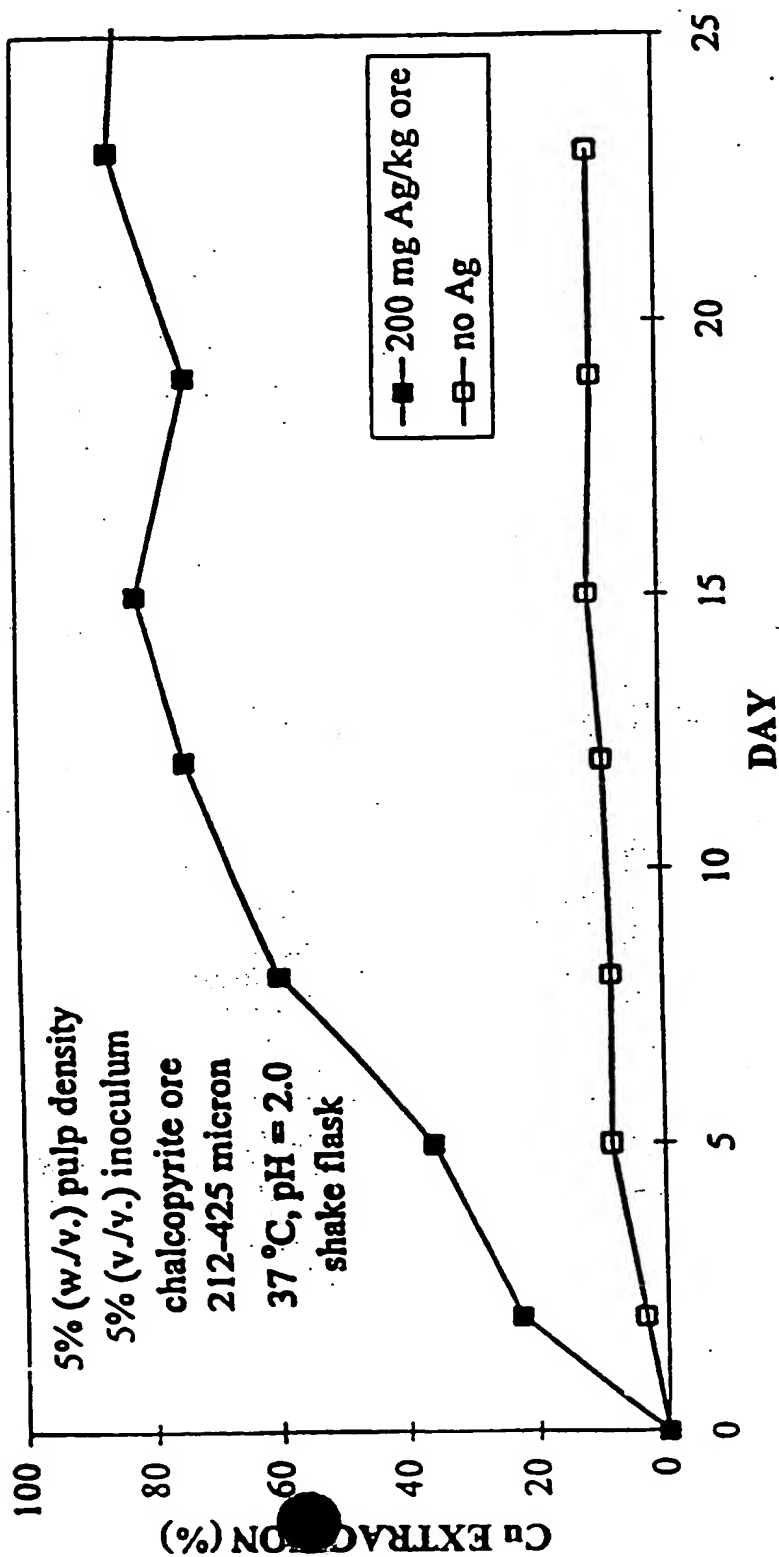


FIG. 1

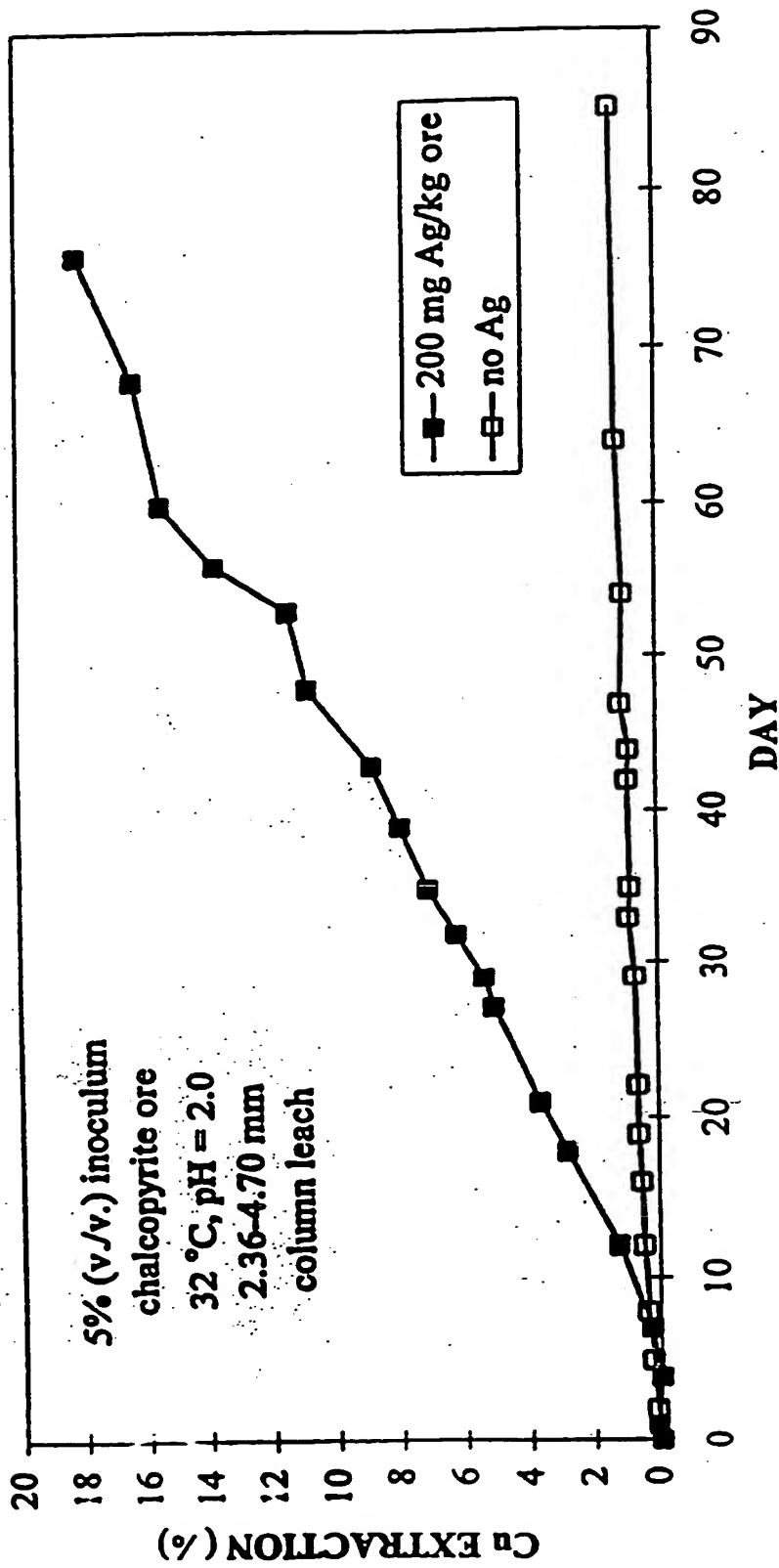


FIG. 2

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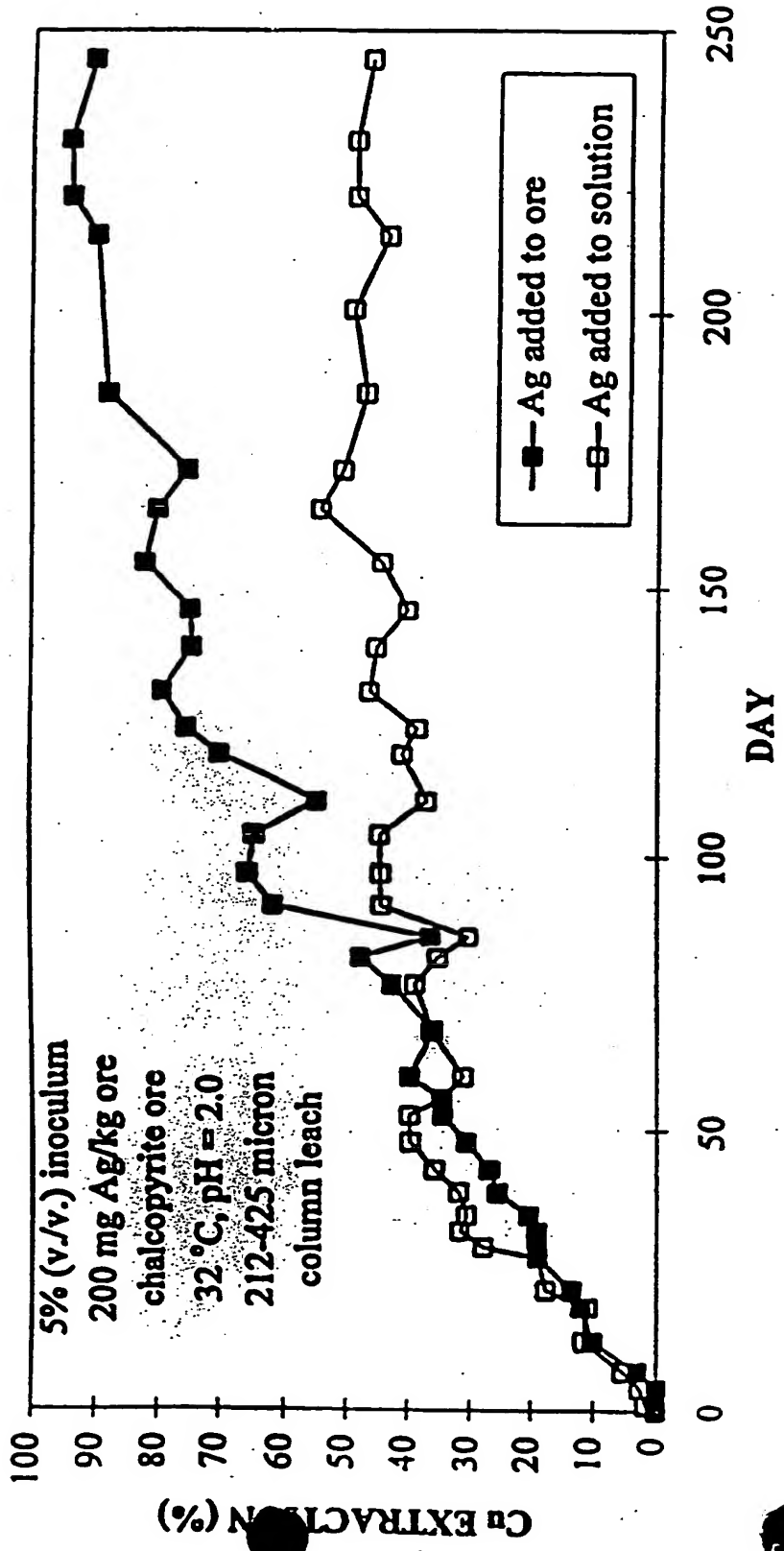


FIG. 3

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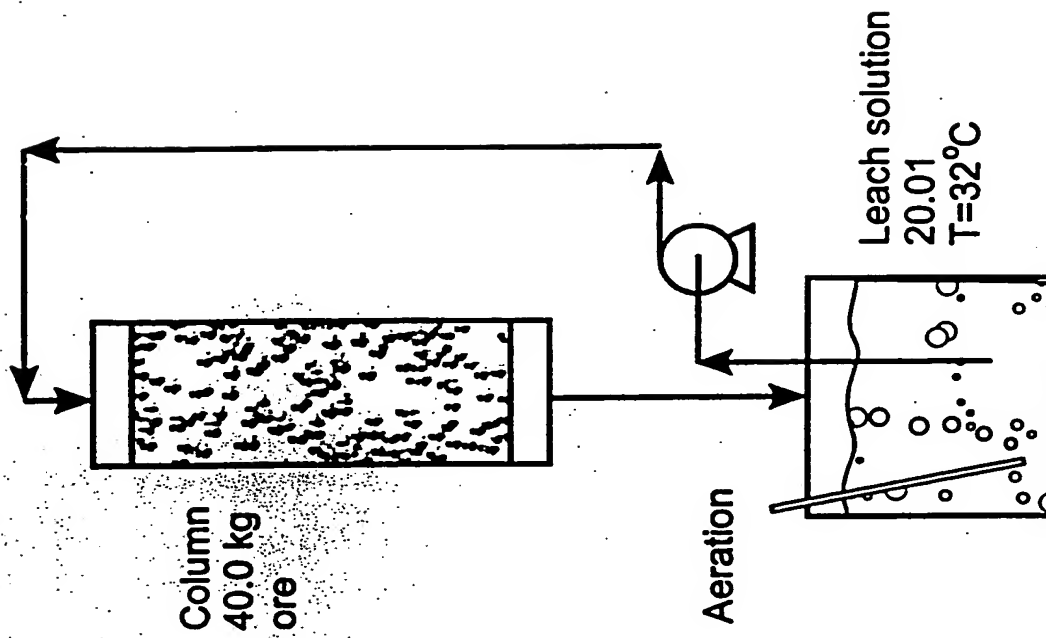
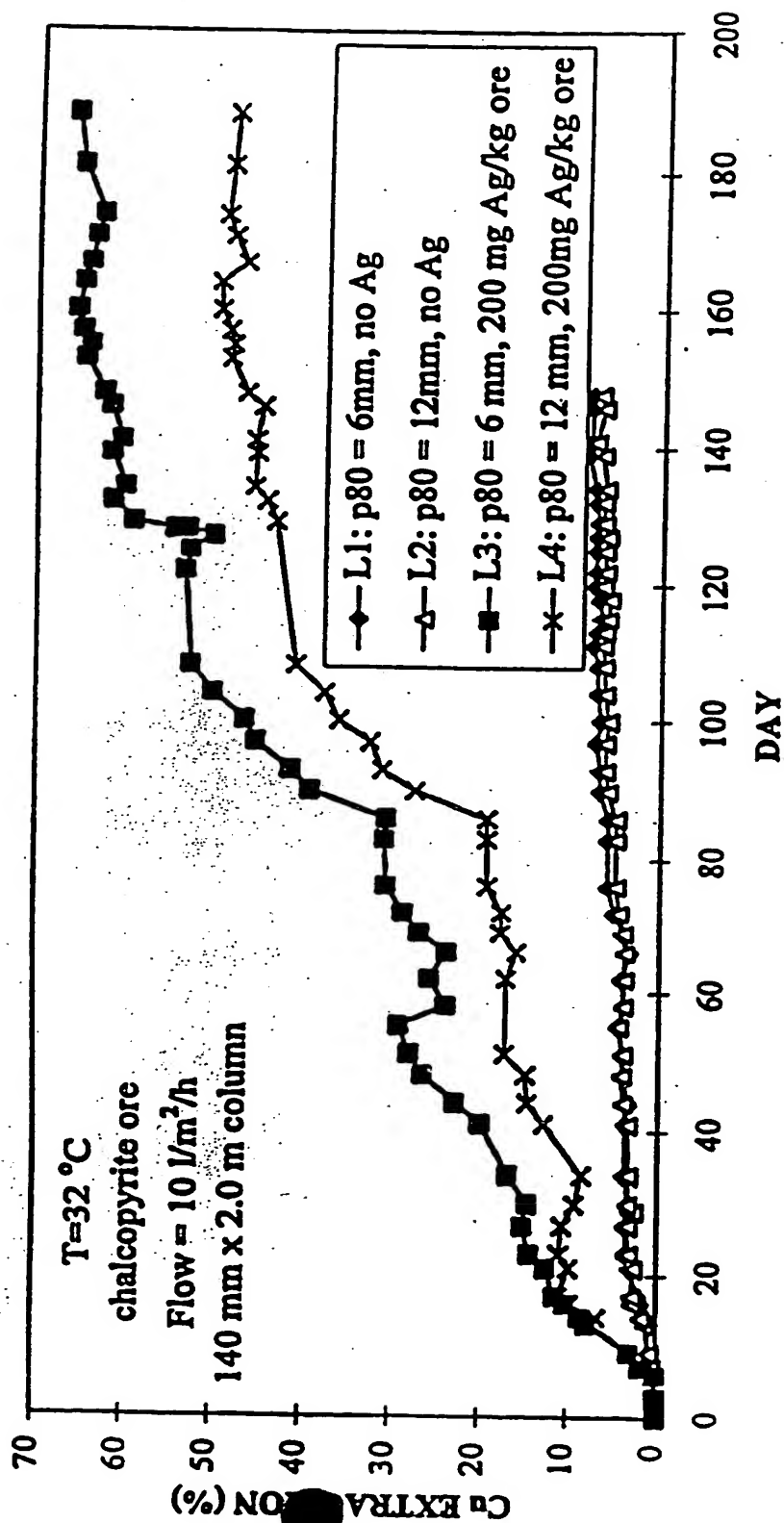


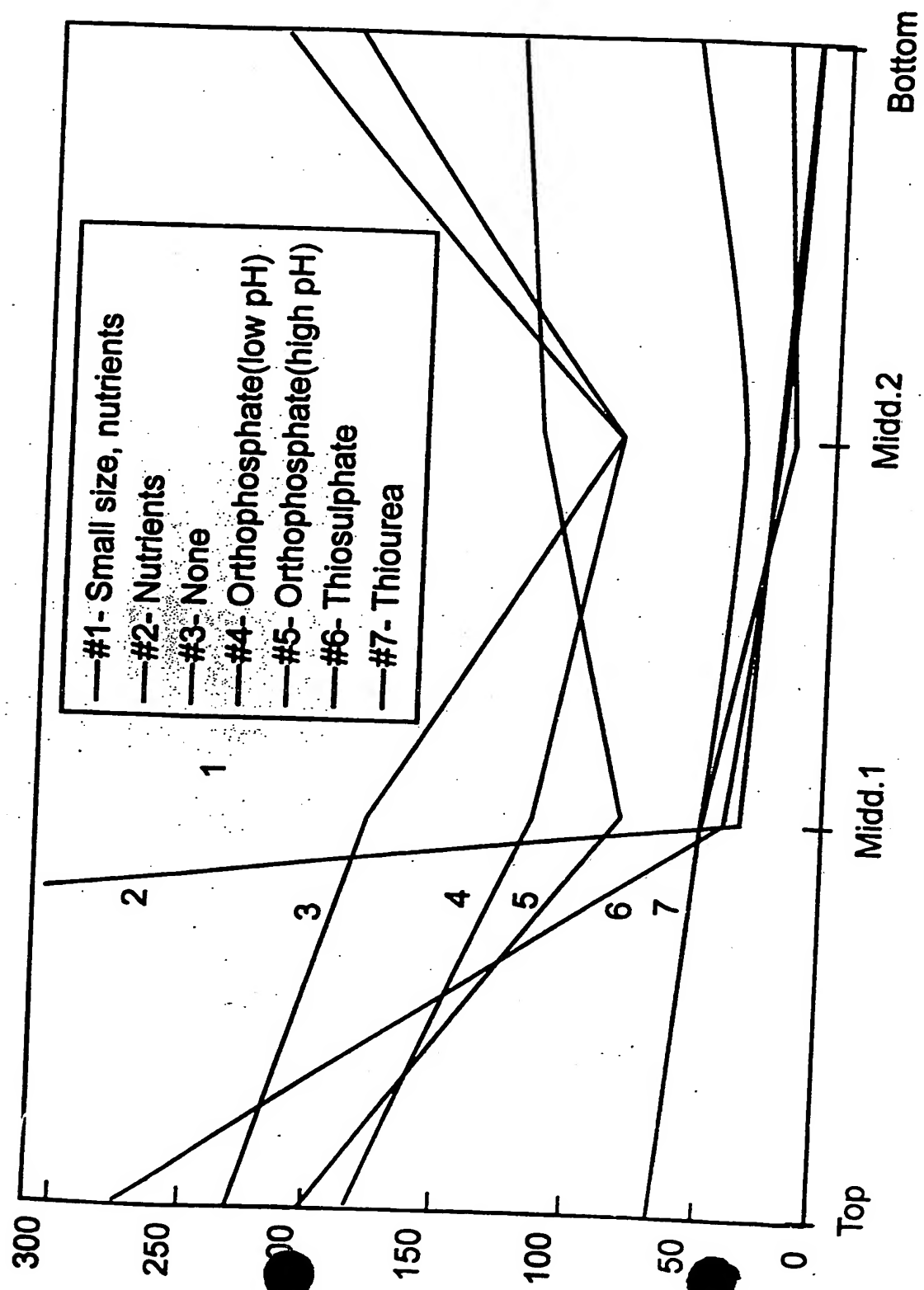
FIG. 4

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ORIGINAL

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POSITION DOWN COLUMN **FIG. 6**